

Heavy Metals Availability and Fractions in Soil Amended with Biosolid Composts

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Abstract

The heavy metals when linked to organic matter have a behavior in the soil that is still little known. This study aimed to evaluate the effect of sewage-sludge-based composts when incorporated in the soil, in relation to heavy metals availability. Five composts were incorporated using sugar-cane bagasse, sewage sludge and cattle manure in the respective proportions: 75-0-25, 75-12.5-12.5, 75-25-0, 50-50-0 and 0-100-0 (composts with 0, 12.5, 25, 50 and 100% sewage sludge). The experiment consisted of 6 treatments (5 composts and a control with mineral fertilization) in randomized blocks with a split-plot design. The control and the treatment of 0% sewage sludge received inorganic nitrogen (N). All the treatments received the same amount of N (8.33 g) K (5.80 g) and K (8.11 g) per pot. Tomato plants were cultivated in 24.0 L pots in a greenhouse in Jaboticabal, SP, Brazil. The concentrations of heavy metals were determined in the soil samples at day 0 after compost incorporation. The higher the sewage sludge doses, the higher heavy metal contents in the soil. Among extractants, Mehlich-1 extracted the highest amount of heavy metals, while DTPA extracted the lowest one. The residual fraction presented the highest heavy metal content, followed by Fe oxides crystalline and amorphous to Cu, Cr and Mn, and Mn oxides, and Fe amorphous to Zn, indicating strong associations to oxides and clays. There were significant positive correlations between Mn contents in the plant and Mn linked to Fe oxide amorphous and crystalline.

INTRODUCTION

Organic composts are used by horticulture farmers all over the world. The efficient use of compost depends not only on the culture to be fertilized, but also on the composting process and on the compost materials. The sewage sludge appears as an alternative to organic compost materials because it is made of organic matters rich in plant nutrients. It can be used as a soil conditioner, too. However, it presents hazardous agents like heavy metals which can severely damage human health, environment, and generally any life source (Revoredo, 2003).

A chemical element behavior in the soil is defined according to its occurrence in different analytical compartments such as soil solution, oxide linked fraction, organic linked fraction, and others. The knowledge about heavy metal equilibrium between its concentrations in each of these compartments has fundamental importance to evaluate its availability and then its toxicity (Reis, 2002). Some studies reported heavy metal availability in areas where sewage sludge was added, revealing organic linkages or DTPA complexant, HCl at 0.1 mol L⁻¹ and Mehlich-3 acid solutions (Oliveira, 2000).

This study aimed to evaluate the application of sewage-sludge-based composts in the soil, in terms of heavy metal availability and forms present in the soil.

MATERIALS AND METHODS

The composts were produced under field conditions, directly on the soil. The experiment was carried out in pots in greenhouse conditions at FCAV/UNESP located in

Jaboticabal, São Paulo state, Brazil.

The organic composts were produced by the standard method of arranging the materials in alternate layers with periodical turning and watering (Kiehl, 1998). Cattle manure, sewage sludge, and sugar cane bagasse were mixed in five composts in proportions of 25:0:75, 12.5:12.5:75, 0:25:75, 0:50:50, and 0:100:0, respectively. The composts obtained were formulated at 0%, 12.5%, 25%, 50%, and 100%, according to the amount of sewage sludge that each compost had received. The chemical characterization of the materials used for composting is presented in Table 1.

After 137 days of composting, a pot experiment was established in randomized blocks including 6 treatments (the different composts and a control with mineral fertilization). Amounts of 300, 501, 430, 367, and 330 g of the composts 0%, 12.5%, 25%, 50%, and 100% respectively, with several concentrations of heavy metals (Table 2), were mixed in a typical haplustox medium texture, contained in 24 L pots (25.34 kg air dried and 2 mm sieved soil) in order to provide 8.33 g N, 5.80 g P and 8.11g K per pot (van Raij, 1997). The mineral fertilization treatment (control) was performed using urea, simple super phosphate, and potassium chloride. The treatment of 0% received 4.61 g N in an organic form (dose equivalent to 10 Mg ha⁻¹) and 3.72 g N in an inorganic form so that all the treatments received the same amount of N, P, and K. Tomato plants cv. 'Carmen', a variety with a determinate growth, were cultivated in pot for 155 days until the 4th raceme appeared when plants were sampled for chemical analysis. Soil samples were collected at 0 days after incorporation in the compost (d.a.i.), and plant samples were collected at the end of the experiment.

Heavy metal content (Cu, Cr, Mn, and Zn), in soil was determined with the extractors HCl 0.1 mol L⁻¹ (Page et al., 1982), DTPA in pH 7.3 (Lindsay and Norvell, 1978), Mehlich-1 (Delfelipo and Ribeiro, 1981), and Mehlich-3 (Mehlich, 1984). The sequential extraction of heavy metals constituted its distribution in the soluble fractions (deionized water), exchangeable [(Mg(NO₃)₂)] 1 mol L⁻¹, organic matter (NaClO 53 ml L⁻¹, in water bath to 100°C per 30 minutes), manganese oxide (NH₂OH.HCl 0.1 mol L⁻¹ (pH 2.0)), amorphous iron oxide (NH₂OH.HCl 0.25 mol L⁻¹ + HCl 0.25 mol L⁻¹, in water bath to 50°C per 30 minutes) and crystalline iron oxide ((NH₄)₂C₂O₄ 0.2 mol L⁻¹ + H₂C₂O₄ 0.2 mol L⁻¹ (pH 3.0) in water bath to 100°C per 30 minutes) and residue (USEPA, 1986). The specific procedure used in each stage, as well the agitation period and the soil/solution rate were carried out as described in Revoredo (2003). The total concentrations of heavy metals were determined in the soil and plant samples by digesting samples with HNO₃+H₂O₂+HCl (USEPA, 1986), and reading metal concentration by an atomic absorption spectrophotometer.

The results were submitted to statistical analysis using subdivides parcels scheme (treatments as parcels and fractions as sub-parcels). When the F test was significant, the averages were compared using the Tukey test (p>0.05).

RESULTS AND DISCUSSION

The composts used in this experiment produced different results in terms of heavy metal availability (Cu, Cr, Mn, and Zn) in the soil, as presented in Tables 3 and 4.

The extractants used to study the availability of heavy metals in the soil resulted in differences in heavy metal contents for the treatments evaluated (Table 3). The Cu available content in the soil, based on extractants, increased when sewage sludge was increased in the compost mixture. The same was observed for Zn and Cr. It happened because sewage sludge has a higher amount of these metals when compared with cattle manure and sugar one bagasse (Table 1). The treatments with 12.5% and 25% of sewage sludge contained higher Mn content than the treatment with cattle manure (Table 2).

Comparing the extractant capacity for Cu and Cr, Mehlich-1 gave higher contents followed by Mehlich-3, HCl 0.1 mol L⁻¹ and DTPA. Ribeiro-Filho et al. (2001) studied the heavy metal availability in contaminated soil with sewage sludge and found Mehlich-1 extracted higher Ni quantities than DTPA. Oliveira and Mattiazzo (2001) also confirmed higher extractant capacity for heavy metals by Mehlich-3 solution than DTPA.

These results, according to de Abreu et al. (1995), are predicted since there is partial heavy metal dissolution in several structures in the soil by the acids that are contained in Mehlich-1 and Mehlich-3 extractors.

The forms of Cu, Cr, Mn, and Zn found in soil (Table 4) were in higher amounts in the residue fraction, strongly resistant to extraction and practically unavailable to plants in a short period of time. These heavy metals held in the residue fraction in the sewage sludge fertilized soils are in agreement with previous results (Reis and Rodella, 2002). However Bertoncini (2002) found most heavy metals linked to the organic matter fraction, followed by oxide, residual and exchangeable fractions.

For Cu, the Fe oxides crystalline and residual fractions were the fractions with the highest amounts of Cu in the soil, which represented 87% of extractable fractions, followed by the fractions linked to amorphous Fe oxide, Mn oxide, organic matter, and others which could not be detected by the method used. While verifying Cu content within the treatments, it was observed that the Cu linked to organic matter fraction differed from the control and other treatments. Cu linked to Fe crystalline oxides was not affected by the treatments. Cu linked to Mn oxides, the control, 50% and 100% treatments resulted in higher values. In the residual fraction, the 25% and 100% treatments gave the higher Cu contents. Cr at Fe crystalline oxides and Fe residual gave an average 98% of all fractions detected in the soil. In sequence, Cr linked to Fe amorphous oxide was detected while the other fractions were not detected by the method used. There was no treatments effect on Cr content, except in the residual fraction, which gave higher contents at 25% treatment.

Mn is linked in the soil to residual, Fe crystalline, Mn oxide, exchangeable, Fe amorphous oxide, organic matter and soluble fractions respectively (Table 4). The compost application in the soil did not interfere in the Mn contents for soluble, exchangeable, organic matter, and Fe amorphous fractions but generated increasing values in the Mn oxide fractions (0% treatment) and residual (0%, 12.5%, and 25% treatments) and was reduced in the Fe crystalline oxide fraction (12.5%, 25% and 100% treatments).

For Zn contents in the residual fraction, the higher contents were found also in the oxide-linked fractions (Mn oxide, Fe amorphous, and Fe crystalline). It was also observed that there was Zn at a lower proportion present in the more soluble fractions (soluble, exchangeable, and organic matter), highlighting the exchangeable fraction due the higher Zn contents than the rest fractions. Between the evaluated treatments, it was verified that the 100% treatment gave higher Zn contents in the evaluated fractions. This fact was predicted due to higher Zn in the sewage sludge (Table 1).

Comparing the sum of all fractions (soluble + exchangeable + organic matter + Mn oxide + Fe amorphous oxide + Fe crystalline oxide + residual) with the total (USEPA, 1986), the Cr and Mn contents did not differ significantly in the treatments. Cu contents were higher in the 25% treatment and Zn in the 100% treatment. Cu and Zn contents were higher in the sum than in the total fractions (Table 4).

There were positive correlations between the tomato plant Mn and Mn found in the amorphous (0.48*) and crystalline (0.55*) fractions and negative correlation between the Mn exchangeable (-0.51*) contents. There was a negative correlation between Fe crystalline oxide and Cu in tomato plants. There was a negative correlation between Mehlich-1 extractor (-0.73*) and Cr in tomato plants.

CONCLUSION

The sewage sludge doses in the composts increased the Cu, Cr and Zn contents in the soil.

The Mehlich-1 extractor had higher extractant capacity for Cu, Cr, Mn and Zn metals than the DTPA.

The higher heavy metal contents were found at residual fraction, followed by the Fe crystalline oxide and Fe amorphous fractions for Cu, Cr and Mn, Mn oxide and Fe amorphous to Zn, indicating strong association with oxides and clays. There were positive

and significant correlations between the Mn in tomato plants and Mn linked to Fe amorphous oxide and Fe crystalline.

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Tables

Table 1. Raw materials' characterization used for composting.

Materials	Zn	Mn	Cu	Cr
	-----mg kg ⁻¹ (dry basis)-----			
Sewage sludge	1099.6	178.1	159.4	309.0
Cattle manure	135.6	186.0	28.7	8.6
Sugar-cane bagasse	10.8	14.5	0.6	4.4

Table 2. Heavy metals concentration in sewage sludge (SW) composts incorporated in the soil.

Composts	Heavy metals			
	Cu	Cr	Mn	Zn
-----mg kg ⁻¹ (dry basis)-----				
0% SW	63.97	83.34	184.56	379.86
12.5% SW	28.75	17.98	203.50	129.05
25% SW	77.65	177.00	114.81	499.18
50% SW	126.24	258.30	160.26	830.69
100% SW	79.69	308.98	178.06	1099.63

Table 3. Heavy metals concentrations available in soil amended with sewage sludge (SW) composts at 0 days after the composts incorporation.

Treatments	Heavy metals							
	Cu		Cr		Mn		Zn	
	-----mg kg ⁻¹ -----							
	DTPA							
Control	0.59	C ¹	nd ²		14.28	B	1.56	D
0% SW	0.57	C	nd		13.18	B	1.66	D
12.5% SW	0.83	B	nd		16.08	A	2.73	C
25% SW	0.94	A	nd		16.97	A	4.93	AB
50% SW	0.95	A	nd		13.68	B	4.61	B
100% SW	1.04	A	nd		13.66	B	5.34	A
C.V. (%)	5.04				4.56		8.81	
Medium	0.82				14.64		3.47	
	HCl 0.1 mol L ⁻¹							
Control	0.71	CD	0.20	A	20.91	A	2.61	C
0% SW	0.60	D	0.07	B	20.00	A	2.75	C
12.5% SW	0.77	C	0.07	B	22.06	A	4.93	BC
25% SW	0.97	B	nd		22.44	A	8.46	AB
50% SW	0.79	C	nd		19.91	A	6.13	BC
100% SW	1.13	A	nd		21.86	A	11.32	A
C.V. (%)	6.75		26.36		5.82		25.63	
Medium	0.83		0.11		21.20		6.03	
	Mehlich-1							
Control	1.02	D	1.01	C	23.19	A	2.66	E
0% SW	0.99	D	0.83	D	22.86	A	3.27	E
12.5% SW	1.32	C	1.05	C	20.19	A	6.01	D
25% SW	1.67	B	1.24	B	24.68	A	9.58	B
50% SW	1.57	BC	1.20	B	22.00	A	8.28	C
100% SW	2.29	A	1.43	A	24.23	A	13.06	A
C.V. (%)	8.34		1.13		18.13		7.11	
Medium	1.48		4.26		22.86		7.14	
	Mehlich-3							
Control	0.84	C	0.60	AB	17.07	AB	2.51	D
0% SW	0.82	C	0.62	A	16.63	B	2.96	CD
12.5% SW	0.96	B	0.57	AB	18.51	A	4.29	C
25% SW	1.13	A	0.56	AB	18.62	A	7.85	A
50% SW	1.09	A	0.52	BC	16.89	AB	5.87	B
100% SW	0.14	A	0.47	C	17.78	AB	6.57	AB
C.V. (%)	4.96		6.57		4.48		11.92	
Medium	1.00		0.56		17.58		5.01	

¹Averages followed by same letter for treatments do not differ statistically by Tukey test (p<0.05).

²nd signify not found by method.

Table 4. Heavy metals sequential extraction in soil amended with sewage sludge composts after the incorporation of the composts.

Fractions	Treatments					
	Control	0% SW ²	12.5% SW	25% SW	50% SW	100% SW
-----mg kg ⁻¹ -----						
Cu						
O.M. ³	0.05 Da ¹	0.03 Da	0.02 Da	0.02 Da	0.02 Da	0.02 Da
OX. Fe A. ⁴	0.53 Ca	0.39 Ca	0.41 Ca	0.48 Ca	0.53 Ca	0.53 Ca
OX. Fe C. ⁵	0.94 Bb	0.92 Bb	1.09 Bab	1.43 Ba	1.24 Bab	1.09 Bab
Residue	1.74 Ab	2.08 Ab	2.57 Aa	2.87 Aa	1.97 Ab	2.82 Aa
C.V. (%) Treatments	14.36				C.V. (%) Fractions	18.94
Fraction Sum	3.25 Ae	3.40 Ade	4.09 Abc	4.78 Aa	3.75 Acd	4.44 Aab
Total (EPA)	2.74 Be	2.87 Bde	3.41 Bbc	3.89 Ba	3.49 Bcd	3.99 Bab
C.V. (%) Treatments	8.19				C.V. (%) Sum vs. Total	7.77
Cr						
OX. Fe A.	0.40 Ca	0.20 Ca	0.16 Ca	0.08 Ca	0.02 Ca	0.02 Ca
OX. Fe C.	12.98 Ba	12.98 Ba	12.64 Ba	12.89 Ba	14.87 Ba	14.82 Ba
Residue	23.90 Ac	24.01 Ac	26.98 Aab	28.1 Aa	25.33 Aabc	2.14 Abc
C.V. (%) Treatments	7.29				C.V. (%) Fractions	12.17
Fraction Sum	37.27 Aa	37.19 Aa	39.77 Aa	41.13 Aa	37.69 Aa	38.97 Aa
Total (EPA)	37.74 Abc	36.93 Ac	38.95 Abc	41.73 Aab	40.21 Abc	44.02 Ba
C.V. (%) Treatments	5.36				C.V. (%) Sum vs. Total	4.94
Mn						
Soluble	1.75 Ea	0.56 Ea	1.77 Da	2.18 Da	2.00 Da	0.93 Da
Exchangeable	6.29 Da	6.08 Da	7.72 Ca	8.44 Ca	6.65 Ca	7.16 Ca
O.M.	0.38 Ea	1.10 Ea	0.31 Da	0.41 Da	0.32 Da	0.35 Da
OX. Mn ⁶	8.78 Cab	10.46 Ca	9.08 BCab	6.80 Cb	7.53 Cab	8.27 Cab
OX. Fe A.	3.09 DEa	2.96 DEa	2.70 Da	2.90 Da	2.54 Da	2.77 Da
OX. Fe C.	17.14 Ba	14.64 Bab	12.08 Bb	12.65 Bb	15.31 Bab	13.18 Bb
Residue	45.04 Ab	45.04 Aa	44.95 Aa	44.11 Aa	38.94 Ab	39.71 Ab
C.V. (%) Treatments	10.07				C.V. (%) Fractions	15.69
Fraction Sum	77.50 Aa	80.08 Aa	78.61 Aa	77.49 Aa	73.26 Aa	72.37 Aa
Total (EPA)	78.19 Aa	77.50 Aa	74.56 Aa	82.19 Aa	73.38 Aa	78.63 Aa
C.V. (%) Treatments	15.31				C.V. (%) Sum vs. Total	12.09
Zn						
Soluble	0.07 Ca	0.08 Ca	0.08 Da	0.11 Fa	0.08 DEa	0.06 Da
Exchangeable	0.16 Cb	0.19 Cb	0.47 Dab	1.10 Eab	0.73 Dab	0.67 Da
O.M.	0.03 Ca	0.05 Ca	0.04 Da	0.05 Fa	0.05 Ea	0.04 Da
OX. Mn	1.43 Be	1.34 Be	2.38 Bd	4.42 Bb	3.20 Bc	5.54 Ba
OX. Fe A.	1.28 Bd	1.51 Bd	2.46 Bc	3.68 Cb	2.79 Bc	5.93 ABa
OX. Fe C.	1.80 Bab	1.72 Bab	1.41 Cb	2.08 Da	1.96 Cab	1.85 Cab
Residue	4.01 Ad	5.18 Ac	6.10 Aab	6.68 Aa	5.87 Ab	6.26 Aab
C.V. (%) Treatments	19.17				C.V. (%) Fractions	15.29
Fraction Sum	8.79 Ae	10.07 Ae	12.92 Ad	18.11 Ab	14.67 Ac	20.35 Aa
Total (EPA)	10.93 Be	12.11 Be	13.64 Bd	18.91 Bb	16.59 Bc	21.13 Ba
C.V. (%) Treatments	7.73				C.V. (%) Sum vs. Total	7.66

¹Averages followed by the same capital letter for fractions and the same lower cap for treatments, do not differ statistically by the Tukey test ($p < 0.05$).

²SW = Sewage Sludge; ³O.M. = organic matter; ⁴OX. Fe A. = Fe amorphous oxide; ⁵OX. Fe C. = Fe crystalline oxide; ⁶OX. Mn = manganese oxide.

